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OPTIMIZATION OF REMOVING OF FREE FATTY ACID CONTEN *JATROPHA CURCAS L.* SEED OIL USING EXPERIMENTAL DESI

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ABSTRACT

An optimization procedure for the removing of free fatty acid content in *Jatropha cu* seed oil was investigated by means of experimental design. After preliminary exper where the extraction rate controlling mechanism was determined, a central composite was applied to evaluate interaction between selected extraction variables such as ext time, extraction temperature, types of solvent and the ratio of volume of solvent to m sample, as well as to optimize these variables in order to obtain the best quality of Ja oil. The quality of oil was determined by the amount of free fatty acid, FFA in Jatrop Predicted and experimental quality of extracted oil were compared and analyzed by Res Surface Methodology (RSM) using *Statistica* software version 6.0. The RSM result s the best value for extraction time, extraction temperature and ratio of volume of solv mass of sample were 4.4 hours; 72°C and 6.5 mL/g, respectively with hexane as solv extract minimum amount of FFA. Pareto chart showed that the ratio of volume of solv mass of sample was the most influence variable.

Key Words: Jatropha oil, extraction parameters, response surface methodology, free acid, Pareto chart

1.0 INTRODUCTION

People in the world are not only depend on petroleum for transportation fuels and heatin but for a long list of products that rarely associate with oil. Petroleum is a non-renew resource and will be depleted. Thus, vegetable oil has become the alternative choice be it was renewable, biodegradable and also non-toxic. There are several non-edible oil species which could be utilized as a source for oil production. *Jatropha.curcas L.* has found as ideal bio-fuel crop, an alternative to fossil fuel. The fatty acid compositi Jatropha oil is similar to other edible oil but the presence of some anti-nutritional factors as toxic phorbil ester renders this oil unsuitable for cooking purpose. Many researchers studied its potential for use as neat oil, as transesterified oil (biodiesel) or as a blend diesel. The calorific value and cetane number of Jatropha oil are comparable to diesel the density is high [1-6].

Solvent extraction is used to extract oil from *Jatropha.curcas* seed, due to its ab to recover almost all the oil, leaving only one percent or less oil in the flakes. In solid-li extraction, assuming there is sufficient solvent present so that all solute entering solid ca dissolved into the liquid and reached the equilibrium state when all the solute is compl

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dissolved [7]. Solid which is the grinded sample and liquid which is the solvent used to extract oil were brought into contact in a period of time. In duration of time were these two phases were intimate, the solvent will extract oil from the solid. After that, the solute and solvent mixture are separated to get a fresh product of Jatropha oil.

In the renewable energy fuels industry, free fatty acid, FFA, is a carboxylic acid or organic acid which has a long aliphatic tail (long chain) that is either saturated or unsaturated. When fatty acids are not attached to other molecules, they are known as free fatty acids [8]. The FFA determines the quality of the oil, the higher FFA value, the lower quality of the oil. The FFA also may corrode automotive parts and these limits protect vehicle engines and fuel tank. In biodiesel production, high FFA content will cause soap formation and separation of products will be exceedingly difficult and thus, the oil will has low yield of biodiesel product [9, 10].

Optimization of the extraction conditions is usually assessed by systematic alteration of one variable while the others are maintained constant. However, this approach is unable to determine interactions between variables and predict extraction conditions. In this respect, experimental designs are appropriate tools for this purpose. Furthermore, these designs allow efficient testing of method robustness [11]. Among these experimental designs, central composite design allow which variables significantly affect each response, determination of optimal conditions as well as to quantify the relationship between the values of some measurable response variables and those of a set of experimental factors presumed to affect the response [12].

2.0 MATERIALS AND METHODS

About 20 kilogram of *Jatropha. curcas* seed is supplied by Nursery Jatropha Plantation located at Kulai, Johor Darul Ta'zim. The experiments in laboratory include sample preparation, extraction process using soxhlet extractor, separation of oil from solvent using rotary vacuum evaporator and FFA determination [13]. The oil was titrated with sodium hydroxide 0.1 N using phenolphthalein as indicator. The FFA was analyzing using *Statistica* software to obtain mathematical model, the optimum value for each parameters and the most influence variable. The mathematical model and experimental result were check by ANOVA.

3.0 RESULTS AND DISCUSSIONS

3.1 Analysis of Central Composite

In order to determine the influencing variables as well as their interaction, a central composite design was carried out. Therefore, sixteen extractions run were required to cover all possible combinations of variable levels as presented in Table 1.

Table 1 Experimental design of extraction process.

Experiment	Extraction time (hour)	Extraction temperature (°C)		Ratio of volume of samp mass of sample (ml/g
		Hexane	Isopropanol	
1	4	60	70	4
2	4	60	70	7
3	4	80	90	4
4	4	80	90	7
5	6	60	70	4
6	6	60	70	7
7	6	80	90	4
8	6	80	90	7
9	6	70	80	5.5
10	5	70	80	5.5
11	3.24	70	80	5.5
12	6.76	52.36	62.36	5.5
13	5	87.64	97.64	5.5
14	5	70	80	2.85
15	5	70	80	8.15
16	5	70	80	5.5

The quadratic model showed relationship between independent variable of extr process, %FFA (Y) with dependent variables which is extraction time (X_1), extr temperature (X_2) and ratio of volume of solvent to mass of sample (X_3). The qu model for %FFA using hexane (Y_h) and isopropanol (Y_i) as solvent are show as below,

$$Y_h = 15.01651 - 1.47462\,X_1 - 0.25111X_2 - 0.8186\,X_3 + 0.08236X_1^2 + 0.0015X_2^2 + 0.07681X_3^2 + 0.01083X_1X_2 - 0.00533\,X_1X_3 - 0.00218\,X_2X_3$$

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$$Y_i = 24.04453 - 0.74039\,X_1 - 0.40453X_2 - 2.23655\,X_3 + 0.03935X_1^2 + 0.00201X_2^2 + 0.07871X_3^2 + 0.00397X_1X_2 + 0.01333X_1X_3 + 0.01462X_2X_3 \quad (2)$$

The critical value is the maximum or minimum value of independent variable and for this study, the critical value was the minimum value of %FFA. From analysis, the critical or optimal value for extraction process at minimum value of %FFA was shown in Table 2. The predicted value of %FFA using hexane as solvent was 0.021049 while for isopropanol was 0.0634921. At optimum condition, the value of %FFA using hexane as solvent was lower than extraction process using isopropanol which indicates hexane is a better solvent compared to isopropanol.

Table 2: Critical value at minimum %FFA.

Solvent	Factor	Observed minimum	Critical value	Observed maximum
Hexane	Extraction time	3.23617	4.40449	6.76383
	Extraction temp	52.36166	72.35575	87.63834
	Ratio	2.85425	6.50665	8.14575
Isopropanol	Extraction time	3.23617	4.66910	6.76383
	Extraction temp	62.36000	69.17106	97.64000
	Ratio	2.85425	7.38802	8.14575

The effect of extraction time, extraction temperature and volume of solvent to mass of sample ratio was analyzed from surface response and contour plot graph from Figure 1 to Figure 6. In Figure 1, at fixed extraction time of 4.4 hours, the percentage FFA of extraction process using hexane decrease with increase in extraction temperature and ratio of volume of solvent to mass of sample. The percentage of FFA was found to decrease with increase of extraction temperature from 52.4°C to 72°C, meanwhile over 72°C, the percentage of FFA increases with increasing extraction temperature. The percentage of FFA was found to decrease with increase in ratio of volume of solvent to mass of sample from 2.85 to 6.5, due to the increase of the driving force for the mass transfer of oil extracted (Figures 1 and 2). However, at ratio more than 6.5 mL/g, the percentage of FFA increases with increasing ratio of volume of solvent to mass of sample.

As observed in Figure 3, the percentage of FFA decrease with increase of extraction time from 3.2 to 4.4 hours, but prolonged extraction time than 4.4 hours, the percentage of FFA increases with increasing extraction time. This indicates that extraction time of 4.4 hours was sufficient to obtain the lowest value of FFA. Thus, for extraction process using hexane as solvent, the lowest percentage of FFA was observed when extraction time was 4.4 hours, extraction temperature was 72°C and ratio of volume of solvent to mass of sample was 6.5.

From Figure 4 at 3.7 hours of extraction time with isopropanol, the percentage of FFA decrease with increase of ratio of volume of solvent to mass of sample from 2.85 to 7.4. This indicates that extraction process had achieved the equilibrium state at ratio of 7.4, where after ratio of 7.4 any additional volume of solvent to mass of sample ratio will not decrease

the percentage of FFA. From Figures 5 and 6, the percentage of FFA had been decrea when extraction time increased from 3.2 to 4.7 hours, meanwhile after 4.7 hours, percentage of FFA increases with increasing extraction time.

In Figure 6, the percentage of FFA decrease with increase in extraction tempera from 62°C to 70°C, but beyond 70°C, the percentage of FFA increases rapidly increasing extraction temperature. The increasing percentage of FFA after 70°C is maybe to the change of chemical or physical properties of J.curcas sample or J.curcas oil du extraction process. The lowest percentage of FFA using isopropanol as solvent was obse when extraction time was 4.7 hours, extraction temperature was 70°C and ratio of volum solvent to mass of sample was 7.4.

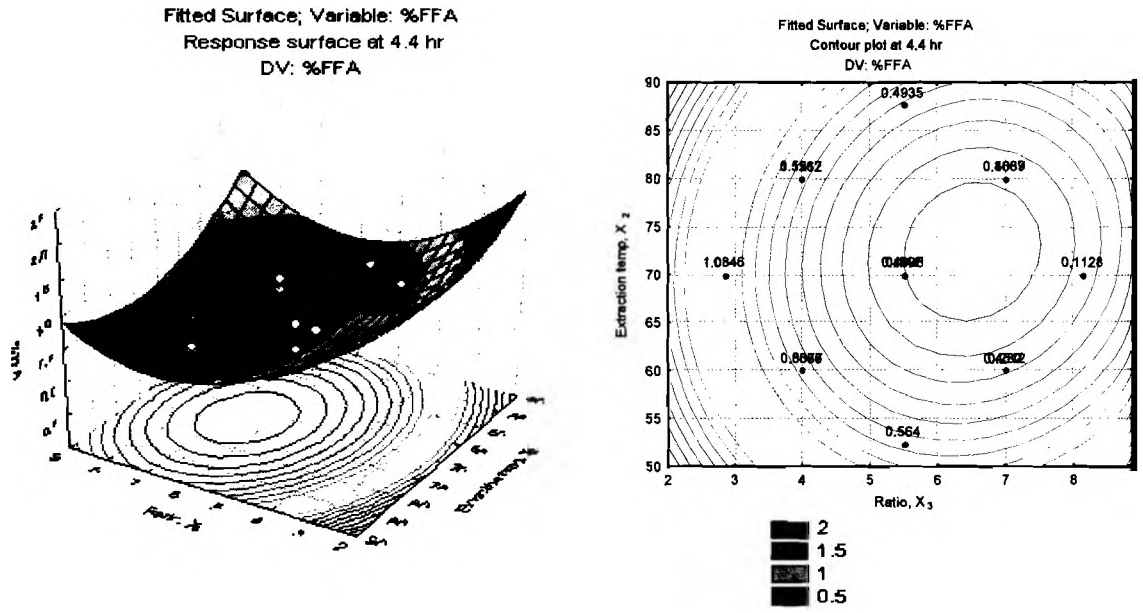

Figure 1 Response surface and contour plot of extraction process using hexane at 4.4

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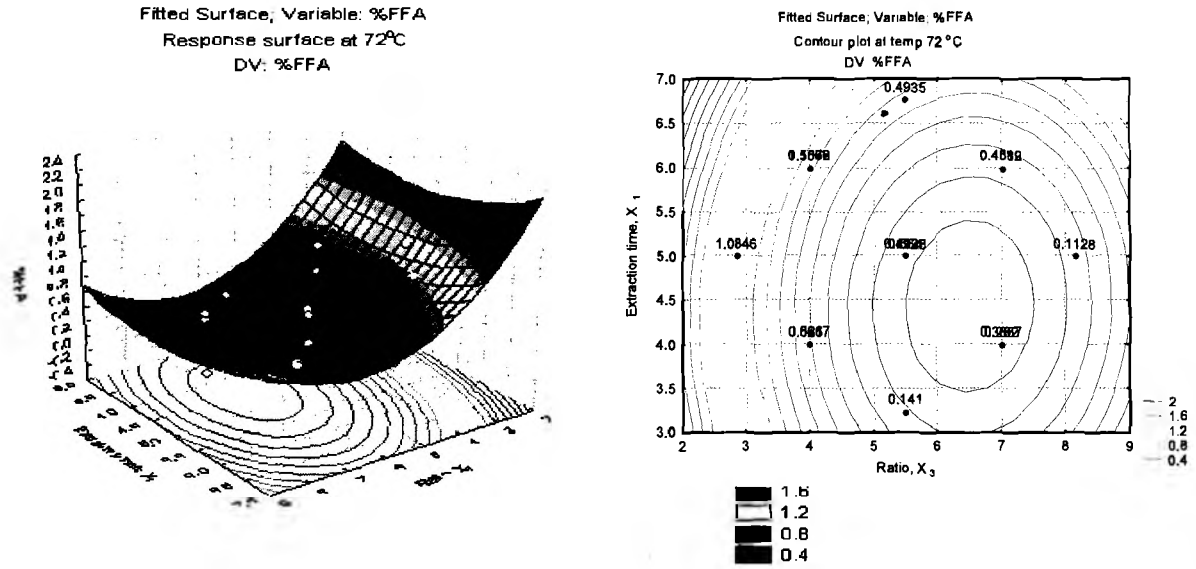

Figure 2 Response surface and contour plot of extraction process using hexane at 72°C.

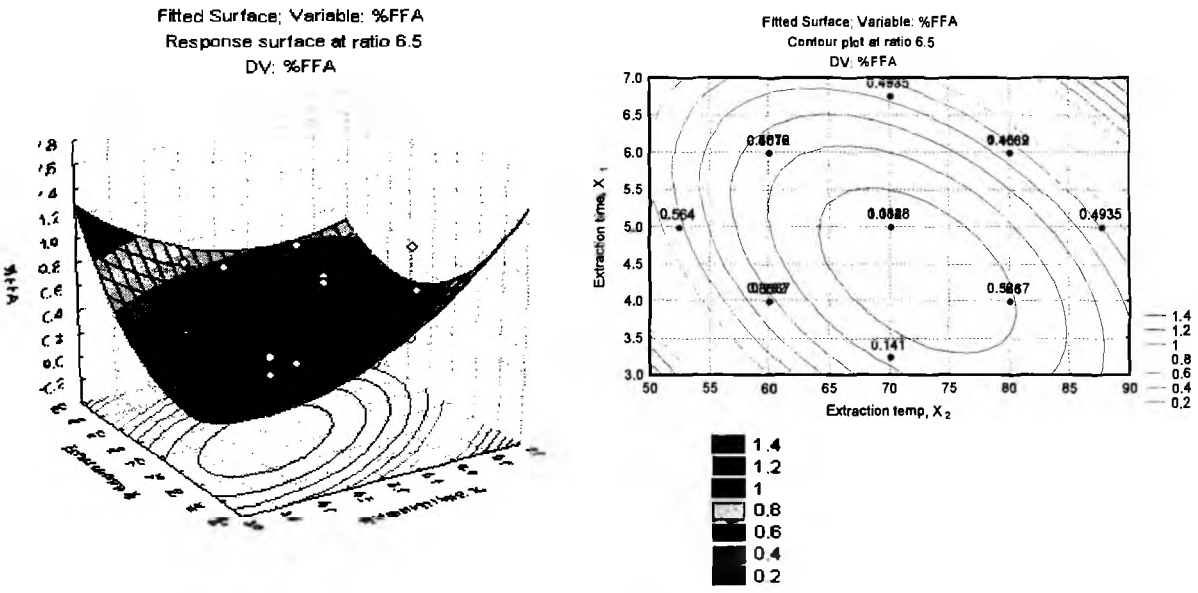

Figure 3 Response surface and contour plot of extraction process using hexane at ratio 6.5.

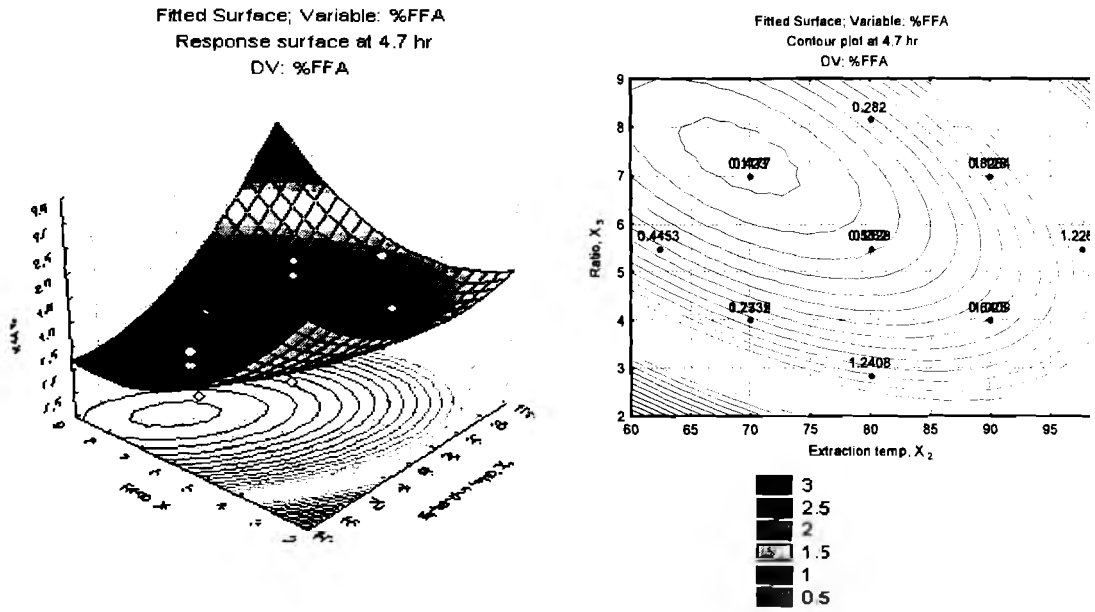

Figure 4 Response surface and contour plot of extraction process using isopropanc hr.

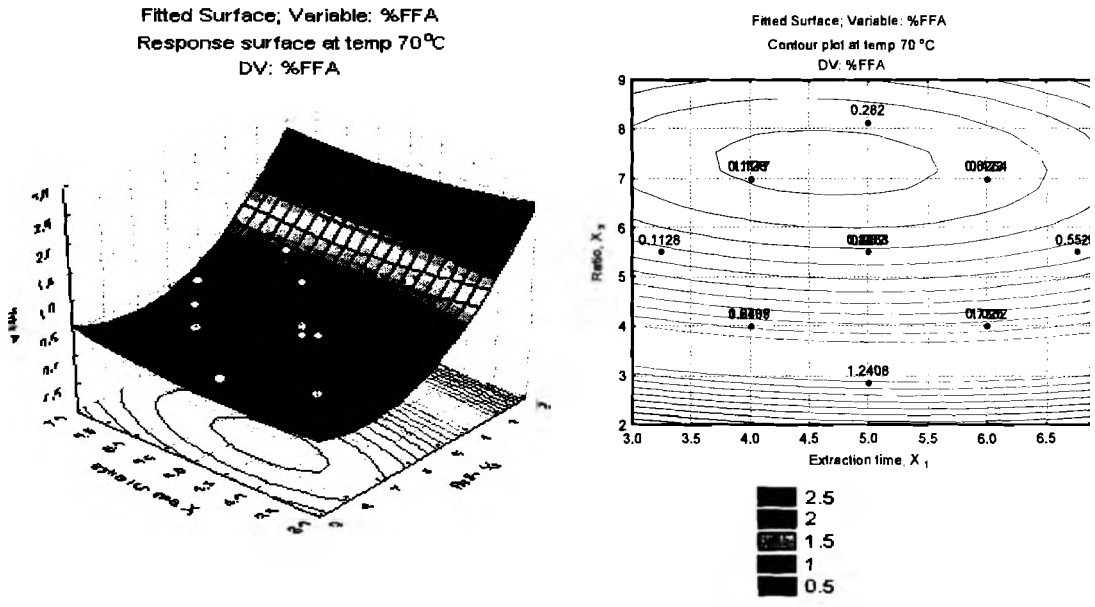

Figure 5 . Response surface and contour plot of extraction process using isopropan 70°C.

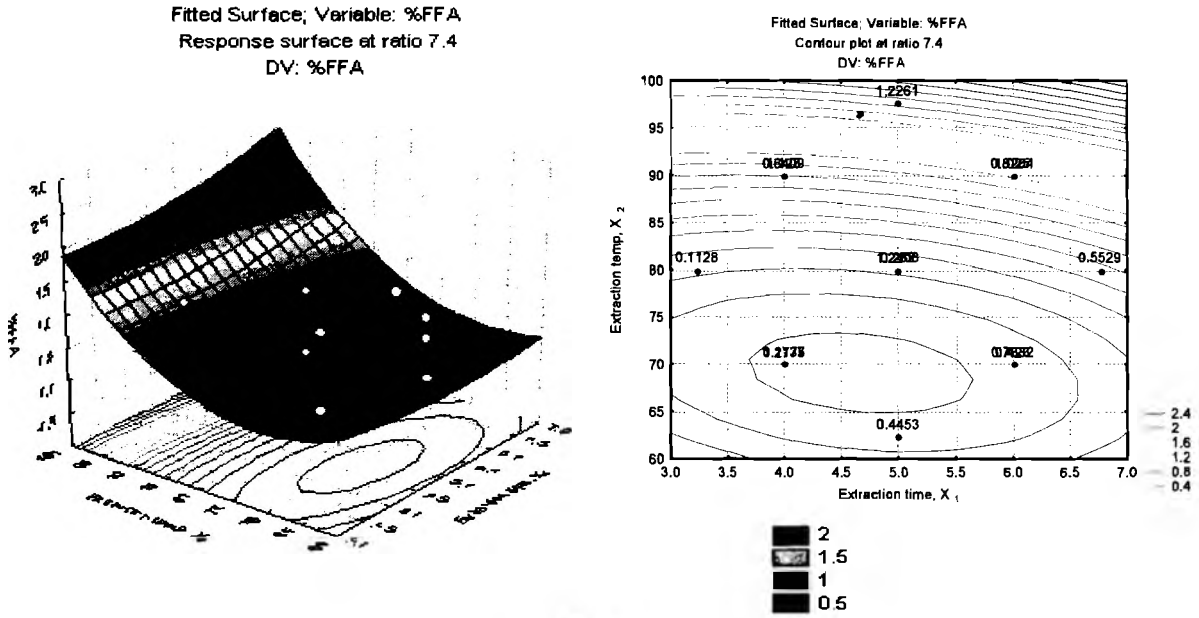

Figure 6 Response surface and contour plot of extraction process using isopropanol at ratio 7.4.

3.2 Pareto Chart

Pareto chart showed the most influence variable in the extraction process. As shown in Figure 7, the most influence variable for extraction process using hexane was the ratio in linear term with value of -4.34575 while the variable that has low effect was the multiply of extraction time with ratio with value of -1.113841. The same result also was observed for the extraction using isopropanol as shown in Figure 8. The ratio in linear term with value of -2.5916 and the variable that has low effect was the multiply of extraction time with ratio with value of 0.1926086. The positive sign indicates that the dependent variable can be operated at maximum level while the negative sign indicates that the dependent variable can be operated at minimum level to get the best response.

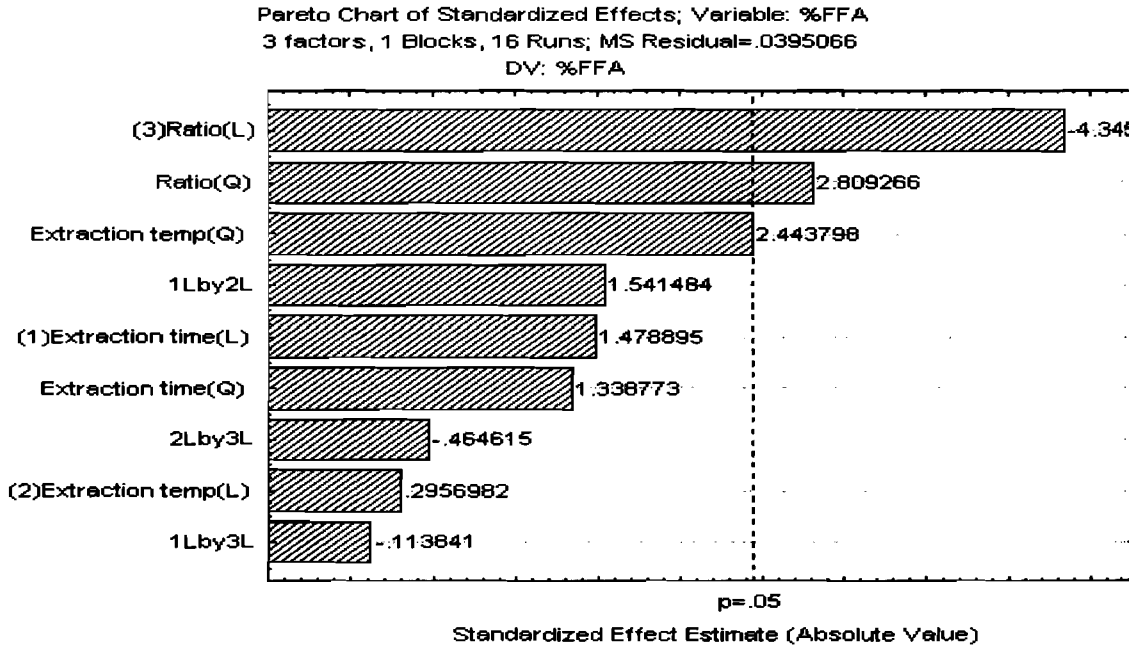

Figure 7 Pareto chart of extraction process using hexane.

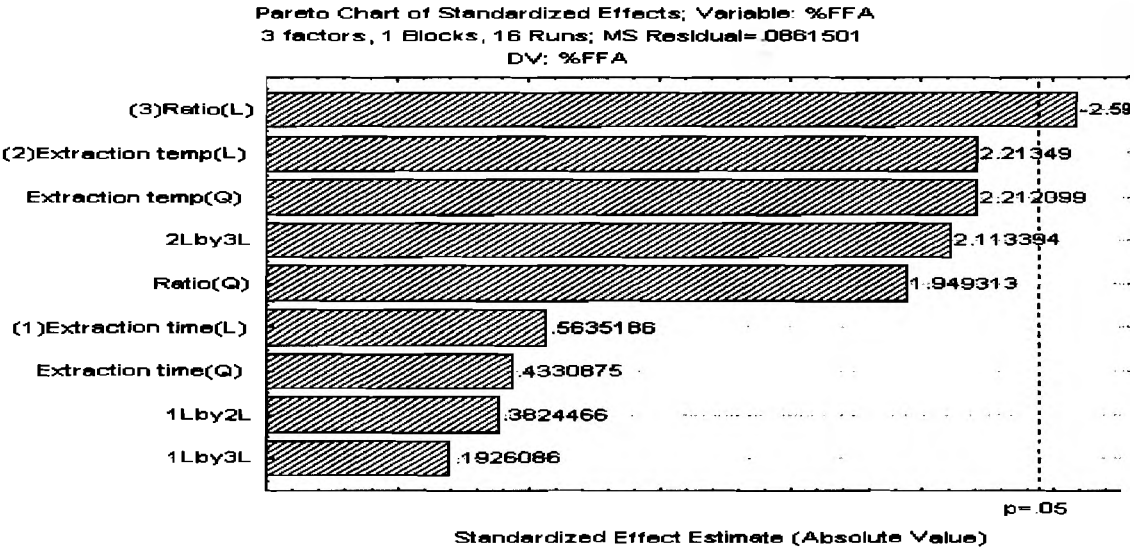

Figure 8 Pareto chart of extraction process using isopropanol.

3.3 Observed and Predicted Value

Observed and predicted value indicates the proportion of total variation w revealed by Coefficient of Determination (R^2) by the fitted model. Graph of observed predicted value of extraction process using hexane and isopropanol was shown in Figu and Figure 10, respectively. From Figure 9 and Figure 10, the point was on the linear li

the graph, meaning that the value from the experiment was fit with the model. From the analysis, R^2 value for extraction process using hexane was 0.84801 while for isopropanol, R^2 was 0.79774. This value indicates that the empirical model was adequate and has good agreement between observed and predicted value where 84.80% and 79.77% of total variation in the response of extraction process using hexane and isopropanol, respectively.

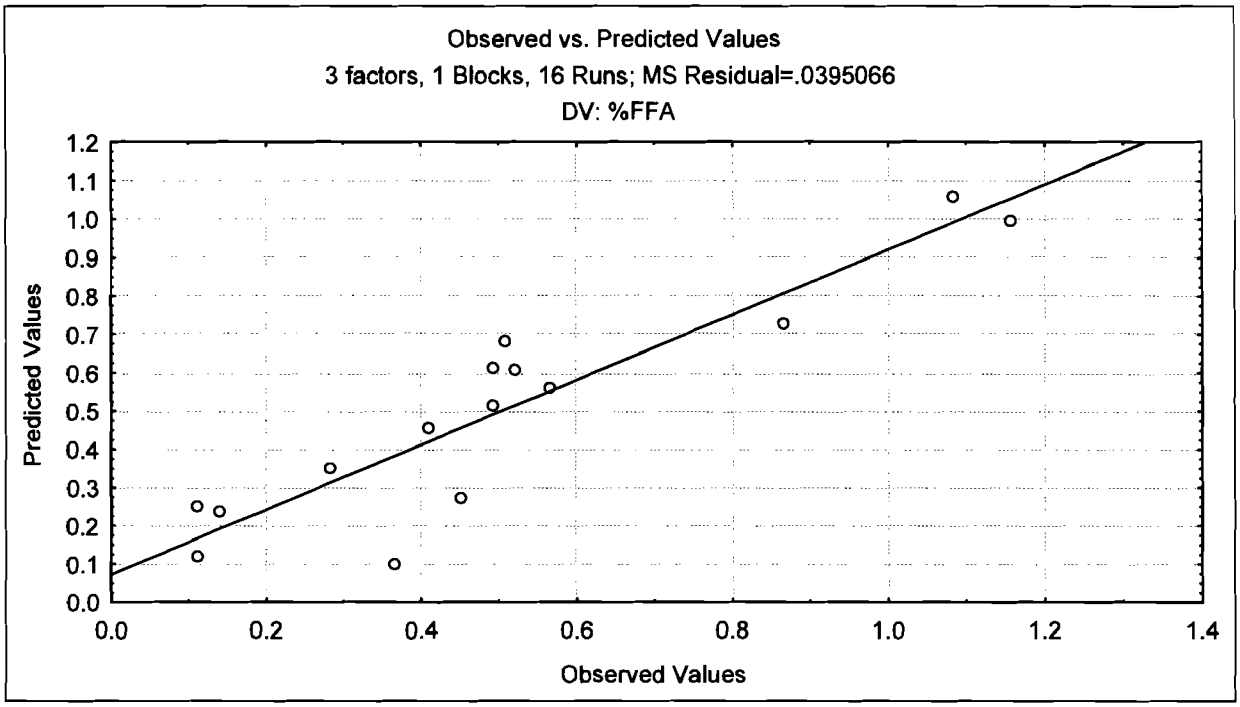

Figure 9 Graph observed versus predicted values of extraction process using hexane.

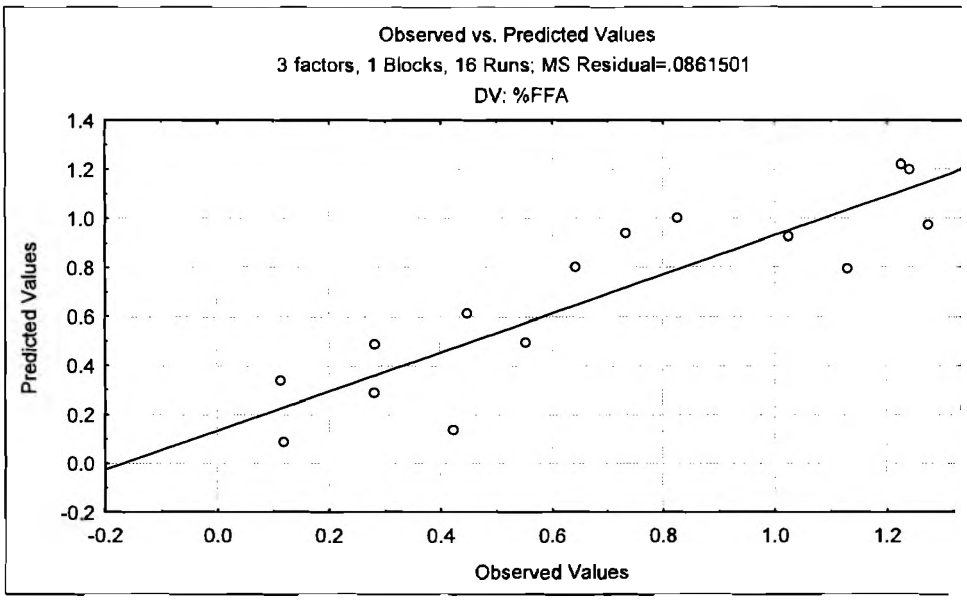

Figure 10 Graph observed versus predicted values of extraction process using isopropanol.

3.4 Analysis of Variance (ANOVA)

Analysis of variance was used to test the significant of the quadratic model by applyi value measurement. F-value is a measurement of variance of data about the mean, bas ratio of mean square of group variance due to error. ANOVA can be determine comparing the F-value of the set of modeling with experimental data. Table 3 s ANOVA result.

The F value was determined from table critical value of F for one-tailed test. T value was determined according to the v_1 which is the degree of freedom of regre presented as nine while v_2, was the degree of freedom of residual presented as six. T value from the table, F_{table} was 0.41. From calculation, the F value for extraction pr using hexane, $F_{H,calc}$ was 13.8978 while F value for extraction process using isopropanol $F_{I,calc}$ was 10.5830. Since both F value from calculation, $F_{H,calc}$, 13.8978 and $F_{I,calc}$, 10. were higher than F_{table}, 4.10, this prove that the model of extraction process using hexan isopropanol as solvent was significant at 95% confident level.

Table 3 ANOVA result for hexane and isopropanol as solvent.

Solvent	Sources	Degree of freedom (dF)	Sum of Squares (SS)	Mean Squares (MS)	F-value	Regression (R^2)
Hexane	Regression	9	4.5279	0.5031	13.8978	0.9757
	Residual	6	0.2169	0.0362		
	Total	15	4.6407			
Isopropanol	Regression	9	8.2005	0.9112	10.5830	0.9857
	Residual	6	0.5168	0.0861		
	Total	15	8.3192			

4.0 CONCLUSIONS

The objective of this study to obtain the best quality of oil at lowest value of FFA has been achieved. The optimum parameter of extraction of oil from J.curcas seed was at 4.4 hour extraction time, 72°C extraction temperature and 6.5 ratio of volume of solvent to mass of sample by using hexane as solvent which yield 0.0210459 %FFA. The most influence variable of oil extraction from J.curcas was the volume of solvent to mass of sample ratio and from analysis of variance (ANOVA), the model was significant at 95% confidence level.

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